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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An experimental determination of the persistence length of an aromatic polyamide-hydrazide, X-500, was undertaken to compare values obtained by light scattering, intrinsic viscosity, and small angle x-ray diffraction. Corrections for molecular weight heterogeneity are well known and should be applied. The status of the treatment excluded volume effects for non-gaussian wormlike chains is not currently adequate.

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## 20.  Abstract continued

We were unsuccessful in an attempt to obtain experimental values of the entropy changes at the crystal-nematic and nematic-isotropic transitions for a thermotropic nematic polymer.  This arose from the difficulty in identifying the nematic phase in highly viscous thermotropic polymers.  Investigations of flow instabilities created by an electric field indicates this procedure may furnish a convenient conformatory test for thermotropic nematic phases.
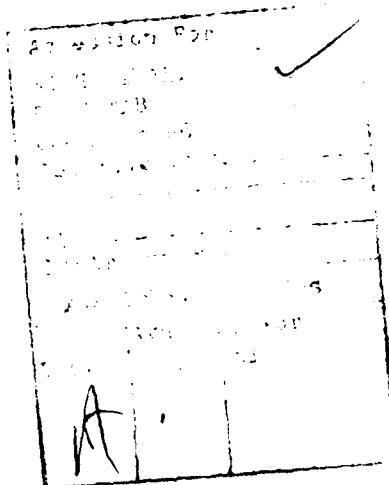
Study of Polymeric Nematic Phases

Final Report

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We proposed to investigate two aspects of nematic phases formed from semi-flexible chain polymers.

1.  An experimental determination of the critical chain extension required for the formation of a nematic phase.

2.  An investigation of the structure of the nematic phase by a thermodynamic study of the nematic → isotropic transition in thermotropic nematic polymers.

Early work of Onsager[1] and Isihara[2] had demonstrated that the origin of the nematic phase in low molecular weight nematics lies in the asymmetric (rodlike or disklike) character of the molecules. The lattice model treatment of Flory[3] showed that rodlike polymers must have a critical axial ratio, and semi-flexible polymers must have a critical chain extension ratio, if a lyotropic nematic phase is to be formed at a given polymer concentration. We proposed to test these predictions by measuring the persistence length of several semi-flexible polymers. This turned out to be a rather popular idea, and results from other laboratories were reported for poly(p-benzamide),[4,5] poly(p-phenylene terephthalamide),[5,6] and a (polyamide hydrazide).[7] These were all polymers we had proposed to study. Examination of these results, and the more extensive collection of data for the polyisocyanates, led us to the conclusion that values obtained by different methods by the same polymer were too discordant. We, in connection with Professor Ciferri's group at the University of Genoa, undertook to determine the persistence length of a single polymer, a polyamide hydrazide, by a variety of techniques, using light scattering,[8] intrinsic viscosity,[9] and small angle x-ray diffraction.[10] It is clear that poor solubility of this class of polymer makes any type of physical chemical measurement difficult. Part of the discordant results is certainly due to neglect it of heterogeneity corrections when different averages, such as $<s^2>_z$ and $<M>_w$, are combined. A second, and more fundamental, difficulty

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is that there is no adequate treatment of excluded volume effects for semi-flexible chains consisting of two few links to behave in a gaussian manner.

The second problem we proposed to investigate involved whether semi-flexible chain polymers in the nematic phase are fully extended, as assumed in his theoretical treatment by Flory.[3] If this is the case, we would expect a much larger change in the entropy at the nematic → isotropic transition for semi-flexible chain polymers, as compared to low molecular weight compounds. We proposed to perform DSC measurements at the thermotropic transition of the Tennessee Eastman copolyesters. A study'' was performed of the co[poly(ethylene terephthalate)-p-oxybenzoate] containing 30 mole percent oxybenzoate units; however, further work in this laboratory showed[12] that this polymer did not form a thermotropic nematic phase. We believe the original objective is worth further effort, and a number of polymers are being synthesized in an effort to find a suitable candidate giving a thermotropic nematic → isotropic transition without an interviewing biphasic region.

Our difficulty with the T2/30 copolymer led to an effort to find more reliable tests for the nematic phase. That misidentification arose from a small amount of polymer haing a higher melting point. When most of the polymer was molten, this crystalline remnant made the fluid phase birefringent. Low molecular weight nematic phases are recognized by the appearance of threadlike structures in the microscope. These features are often missing in polymeric nematics, unless the molecular weight is quite low. A second diagnostic test involves DSC. However, this can be difficult to interpret if there are polymorphic modifications with different melting temperatures. Also, some nematogens exhibit a biphasic structure over a wide temperature range, and the enthalpy change associated with the transition to the isotropic phase occurs over such a span of temperature as to be lost if the DSC instrument does not have high sensitivity and a stable baseline. It is our opinion that x-ray diffraction

does not permit a very certain identification of a nematic phase in polymers. The effect of electric or magnetic fields appeared to offer promise. The need to maintain a high sample temperature for thermotropic nematogens led us to the conclusion that electrical field effects could be more easily investigated. We found[13,14] that application of an electric field led to flow instabilities, and that the hydrodynamic flows became organized in well known patterns, even for polymeric nematics. We were able to observe Williams domains and the variable grating mode patterns, but not chevrons or the dynamic scattering mode. As might be expected from the high melt viscosity, the formation time for these structures is of the order of an hour for polymers, as compared to tenths or hundredths of a second for low molecular weight nematics. We also observed a high field turbulence which appeared to be characteristic of the nematic phase, and had a formation time on the order of a minute. This has the desired features of a confirmatory test for thermotropic polymeric nematic phases.

There are a number of questions concerning electric field effects which we hope to answer by future work. We need to demonstrate whether this test is universal or, if not, the types of structures for which it is applicable. Secondly, all of our work has involved direct exposure of the polymers to the electrodes. Hence, we do not know whether we are dealing with an electric field effect, or whether charge injection at the electrode is essential for the process. Finally, insulated electrodes may allow application of the same procedure to lyotropic nematics. The high conductivity of most of the solvents prevents examination of this category using exposed electrodes.

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